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利用超分子化学与高分子力化学构筑新型超韧力响应聚合物材料的探索

张欢

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题名页

利用超分子化学与高分子力化学构筑新型超韧力响应聚合物材料的探索

Supramolecular Chemistry and Polymer Mechanochemisty to Access Strong, Tough, and Mechanoresponsive Polymers

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摘要

内 容 摘 要

本论文针对人工合成聚合物无法兼具强度和韧性并且在机械力作用下无响应功能的缺点，提出利用超分子化学仿生增强增韧聚合物材料和利用高分子力化学来赋予材料力响应功能的方法。本论文的工作涵盖了以下几个方面：

1.利用金属配体相互作用和氢键相互作用成功增强增韧聚合物材料。利用疏水相互作用增强水凝胶的力学性能。

2.与他人合作，利用超分子相互作用成功制备可自修复的高分子材料。

3.与他人合作，成功制备了螺吡喃类力色团，并研究了其在聚合物本体材料中的力致变色行为和超分子作用的相互关系。首次提出超分子作用可增强力色团的活化。

4.证明螺吡喃类力色团可作为分子探针来研究聚合物材料的断裂行为。

5.设计了基于 1,2,3 三唑环的力色团分子，并研究了其力致释放特定小分子的功能。

6.将超分子化学、仿生设计、高分子力化学结合，成功制备具有超强力学性能和力响应功能的聚合物材料。

关键词： 超分子化学，高分子力化学，力响应聚合物，聚合物力学性能，自修复材料

英文摘要

Abstract

It is a great challenge to polymer science to develop polymers that can perform under high mechanical loads with the accommodation of large strain and response to mechanical force in useful and productive manners. Herein, we report the use of supramolecular chemistry and biomimetic design to reinforce the mechanical properties of polymeric materials. We also explore polymer mechanochemistry to develop mechanoresponsive materials. This thesis covers the following aspects:

1. We utilized metal-ligand and hydrogen bonding interactions to reinforce and toughen polymers. We prepared strong and tough hydrogels by simply incorporating hydrophobic monomers.

2. We fabricated self-healing polymers and conductive nanocomposites based on supramolecular interactions.

3. We synthesized spiropyran (SP) mechanophore and explored the correlation between the activation of SP and the supramolecular interactions in bulk. We for the first time proposed that supramolecular interactions can enhanced the mechanical activation of mechanophores.

4. We demonstrated that SP can be used as a molecular force probe to study the fracture mechanism of polymers.

5. We explored the force-induced release of target molecules using a 1,2,3-triazole mechanophore.

6. We combined supramolecular chemistry, polymer mechanochemistry, and biomimetic design to prepare mechanoresponsive polymers with strong and tough mechanical properties.

Keywords: Supramolecular chemistry; Polymer mechanochemistry, Mechanoresponsive materials, Mechanical properties; Self-healing polymers

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1. Introduction

1.1 Polymer Mechanical Behavior and Chain Fracture

Polymer Mechanical Behavior. Polymers are important class of materials and polymer products are indispensable in our daily life such as plastic bags, rubber sears, and fishing lines, to name a few. The mechanical property of polymers is a critical issue in their applications.[1] Polymers exhibit an extraordinary range of mechanical responses, which can be either soft and elastic or hard and brittle, depending on their chemical and physical structure of the polymer chains.[2] Generally, polymers can be classified into three category: thermoplastic, thermoset, or elastomer. A thermoplastic is a plastic which is pliable or moldable above a specific temperature and becomes a solid state upon cooling. The mechanical property of thermoplastic polymers highly depends on the chemical structure of the monomer, the molecular mass, chain alignment, chain entanglements, supramolecular interaction between the chains, and degree of crystallinity.[3] A thermosetting resin, on the contrary, is usually liquid or malleable at low temperature but becomes a solid after curing at high temperature.[4] Once cured, a thermoset resin cannot be melted to change its shape. Thermosets are usually amorphous and their mechanical response is influenced by the cross-linking density. An elastomer (e.g., rubber) is a lightly cross-linked three dimensional network with extreme deformability.[5] The cross-linking points can be formed by either covalent bonds or supramolecular interactions or both.

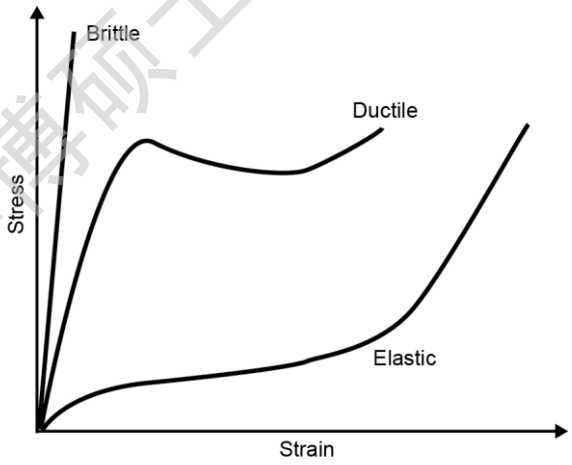

Fig. 1.1 Schematic illustration of the mechanical responses of polymeric materials. It varies from elastomeric to brittle.

Unlike ideal solid that is purely elastic (Hookean solid) or ideal liquid that is purely viscous (Newtonian liquid), the mechanical responses of most polymers are viscoelastic (having both viscos and elastic components).[6] Therefore, the response to mechanical force depends not only on the structure of the polymers but also on time scale and temperature. For example, at temperatures above the glass transition

temperature (T_g), polymer chains have enhanced mobility, promoting macroscopic flow (Fig.1.1). However, below T_g, the mobility is restricted at segmental length scale and the material is brittle and glassy (Fig.1.1). The mechanical property of polymers is also influenced by how fast the force is exerted (strain rate). Faster strain rate limits the movement of the chains to dissipate strain energy and favors a more glassy response. However, slower strain rate often leads to viscous response or rubber-like behaviors.[7]

Polymer Chain Fracture. The failure of polymers can occur at relatively low stress levels below the ultimate strength because of long term stress, cyclic stress, flaws and defects, and cracking agents.

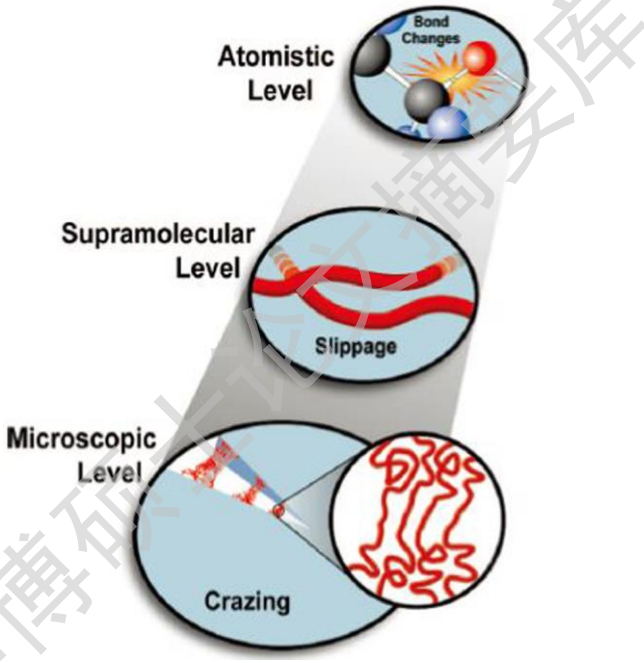

Fig. 1.2 Diagram depicting the hierarchical levels of mechanochemical change at various length scale.[1] Adopted with permission from ref 1. Copyright 2009 American Chemical Society.

The fracture of polymer materials are multiscale phenomena (Fig.1.2). At macroscopic level, failure can proceed from either brittle fracture or ductile fracture. In brittle fracture, no apparent plastic deformation takes place before fracture and the crack propagates rapidly with low energy released. Ductile fracture is preceded by substantial plastic deformation. At the microscopic level, voids, cavitation, yield or crazing, and crack formation take place along with large scale viscoelastic deformation.[8] At supramolecular length scale, chain slippage, disentanglement, strain induced crystallization[9], and chain unravelling occur, generating deformations at the molecular level. The stretching of the bond, the bending of the valence angle, and the rotating of dihedral angle result in a redistribution of the electronic densities on the molecular orbitals and eventually the chemical effect known as bond

disassociation.[10] In polymers, the ultimate mechanical performance are essentially related to the break of carbon-carbon bonds.

To enhance the mechanical properties of artificial polymers, dissipative mechanisms ranging from macroscopic level to supramolecular level can be introduced to delay the scission of covalent bonds. This involves two concepts: "sacrificial bonds" and "hidden length", which are the main principles to design strong and tough polymeric systems.[11-12]

The devastating force which breaks the carbon-carbon bonds during deformation is regarded as unproductive and should be avoided in the past. However, recently advances in the area of polymer mechanochemistry point out the feasibility to use mechanical force to trigger chemical reactions of force-sensitive molecules (*mechanophore*) to acquire desired functions. Mechanophore offers researches the way to prepare mechanoresponsive polymers that are previously inaccessible.

1.2 Biomimetic Design Based on Supramolecular Chemistry

Through continuing diversification and specialization, nature has evolved many sophisticated biomacromolecules, including skeletal muscle protein titin,[13-15] red cell spectrin,[16] and spider silk,[17] which unfold superior mechanical properties to their anthropogenic counterparts. These biopolymers widely exist in muscle, seashell, and bones.[18]

A very prevalent strategy nature often adopts to tough mechanical performance is the use of non-covalent weak forces (i.e., supramolecular interactions) in addition to covalent bonds. These non-covalent interactions that stabilized a folded protein structure and, under applied load, rupture prior to the covalent bonds in the protein backbone, are termed as "sacrificial bonds". These sacrificial bonds not only provide extra toughness to the material, but also lead to molecular self-repair at strain-free state by reforming the physical bonds.[19] In protein-based systems, hydrogen bonds are one kind of sacrificial bonds. Although very weak (2.1 – 21 kJ mol^{-1}[20]), hydrogen bonds offer incredible resistance to load if they are abundant. Recently, metal-ligand interactions was found to serve as reversible sacrificial bonds as well.[21] Unlike hydrogen bonds, metal complexes have the benefit of an increases breaking force, while still being able to reform easily.

Fig. 1.3 Repetitive modular mutidomain structure of titin that has sacrificial bonds and hidden length.[22]

Another strategy nature likes to use is "hidden length". As a result of the rupture of sacrificial bonds, hidden length are released to relief the local high stress so as to protect the protein backbone. The hidden length is defined as the part of the molecule

that was constrained rom stretching by the sacrificial bond.[23] The combination of hidden length with sacrificial bonds are proved to be the two key factors to enhance the mechanical performance of materials. The secondary structures in protein-based materials such as α-helix, β-sheet, and polyproline type II are typical examples that have both sacrificial bonds and hidden length. In Fig.1.3, a multidomain modular structure of titin is illustrated.[22] Each domain is held by supramolecular interactions and upon rupture of the physical bonds, hidden length can be released sequentially to protect the backbone, leading to excellent combination of strong, tough, and elastic properties of this protein. This strategy is exploited by many other nature materials such as hair keratin, hagfish slime, marine snail egg cases, and mussel byssus.[12, 24]

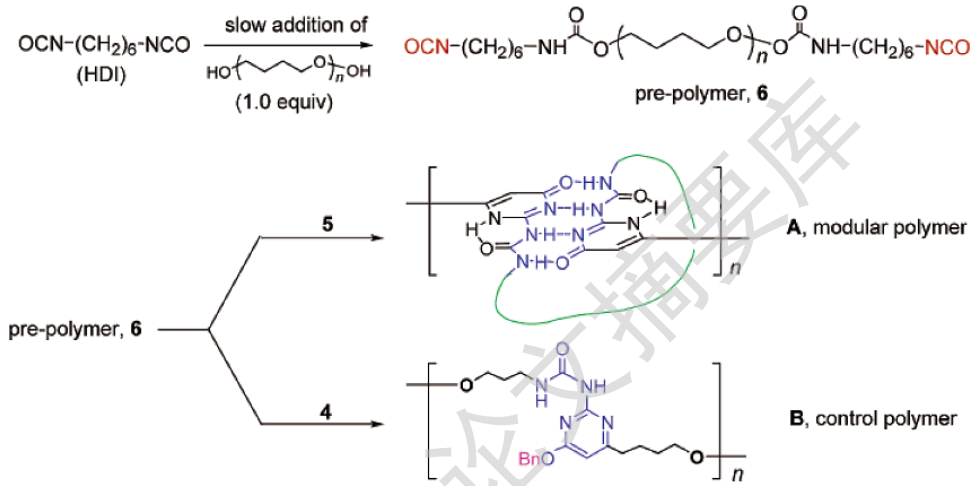

Fig. 1.4 The design of dimeric hydrogen bonding systems as the building blocks of biomimetic polymers.[22]

Inspired by titin, Guan and his co-workers took the ease of dimeric hydrogen bonding systems (Fig.1.4) as the building blocks of the modular domains and have succeeded in developing a series of its synthetic analogues which combined excellent mechanical, self-healing, and shape memory properties.[12, 18, 22, 25-27]

1.3 Polymer Mechanochemistry

History of Polymer Mechanochemistry. Polymer mechanochemistry was born as early as the concept of macromolecules. Indeed, the first reports on flow-induced degradation of polymer were given by Staudinger (Nobel Prize, 1953),[28-30] one of the trailblazers of macromolecular science. The increasing demands of polymeric products from the middle of the last century called for the study of their behavior under mechanical processing. Early work suggested that the depolymerization of the chains during ball-milling, drilling, slicing, or sawing can advance by homolytic cleavage (two free macroradicals[31-32]), heterolytic cleavage (two macromolecular ions with opposite charges), or intramolecular disproportionation (two stable macromolecular fragments).[33]

Mechanical degradation of polymers in solution was also implemented. The coil-like character of macromolecules gives them unique dynamics in the flow field

compared to small molecules. In the 1940s, Kuhn and Frenkel performed experiments in simple shear flow.[34-35] They believed a simple shear flow with velocity gradient transverse to the flow direction, is sufficient to degrade polymer chains. The mechanical stability of macromolecules in solution is thus referred to as "shear stability". However, theoretical work in the early 1960s showed that only elongational flow with velocity gradient parallel to flow direction is able to largely extend the coil.[36-38] After de Gennes' (Nobel Prize, 1991) prediction of the coil-to-stretch transition (CST) of polymer chains in 1974,[39] the experimental progress hasted. These works revealed a minimum molecular weight M_{lim} required for chain cleavage.[33] Odell and Keller's elegantly designed flow experiments[40-41] demonstrated the connection between CST and the most basic properties of the polymer chain. Their outstanding work led the subject into the modern era with quantitative studies.[1]

In the last decade, researchers take advantage of the molecular strain generated during CST to trigger the chemical reaction of certain organic molecules (called *mechanophore*). Moore, Craig and their co-workers reported breakthrough works in this avenue. Examples include the use of mechanical force to unveil prohibited reaction pathway[42] or to prolong the lifetime of the diradical intermediate.[43] These subversive works give impetus to develop mechanoresponsive materials and mark the beginning of a new epoch in polymer mechanochemistry.

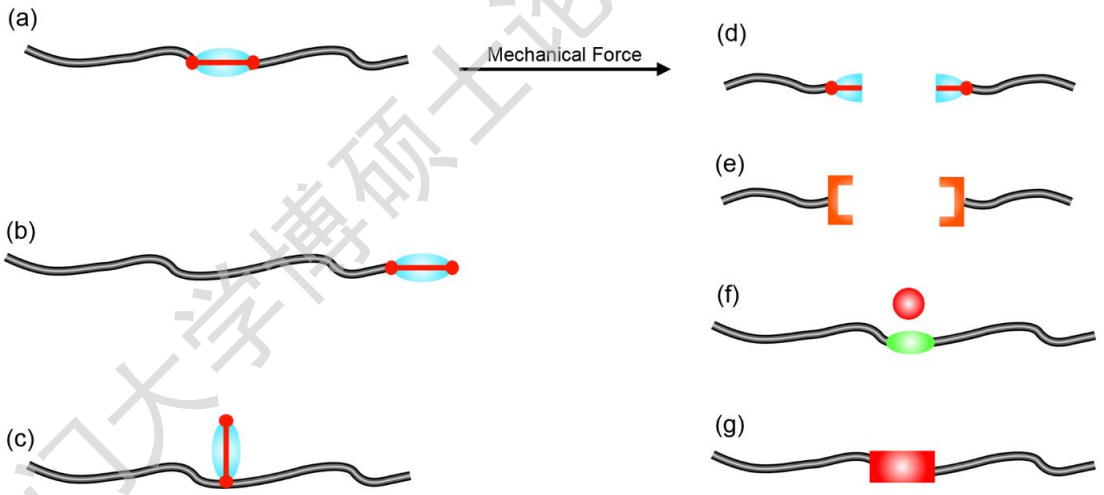

Fig. 1.5 Schematics of a mechanophore embedded in a polymer chain.[1] (a) The mechanophore is in the mid of the chain. (b) Control polymers having a mechanophore at the chain terminal or (c) as a pendent group. The red stick in the mechanophore represents the active site. Possible responses to force for a mechanophore: (d) selective scission; (e) cycloreversion; (f) release of small molecule; (g) isomerization.

Activation of Mechanophore by Polymer. A mechanophore (blue in Fig.1.5a), is a strategically designed chemical entity, which responds to mechanical force in predictable and useful manners (Fig.1.5d to f). The polymer strand here acts as an actuator to transmit macroscopic force to the target. So the mechanophore should be

incorporated into the mid of the chain with its activation site spanning along the chain contour (Fig.1.5a). [1, 42, 44] Examples of mechanochemical reactions include homolytic scission of weak bonds (diazo[45]), electrocyclic ring-opening (benzocyclobutenes,[42] spiropyrans,[44, 46-57]*gem*-dichlorocyclopropanes,[58-61] *gem*-difluorocyclopropanes,[43, 62] epoxide,[63] and 1,2-dioxetanes[64]), cycloreversion reactions (cyclobutane derivatives[65-69], Diels-Alder adducts[70-71], and 1,3-dipolar adducts[72-73]), dative bond scission[74-76], and flex-activated reactions[46, 77-78], as recently reviewed by Bielawski.[79]

The rational design of mechanophore offers a new avenue towards intelligent polymers which response to mechanical force in incredible ways.[80] Imagine the following pictures. A polymer can send a warning signal by changing its color on deformation.[44] Close to mechanical failure, the force breaks the purposely designed bonds to relieve the local stress by releasing "hidden length" (molecular stress relief)[66-67, 81] and/or to redistribute the local force by interchain cross-linking (self-strengthening).[82] Once the chain breaks, it sends a second signal[64] and the outcomes (radicals or other small molecules) can catalyze latent chemical reactions.[61, 83-84] Even if the material fails, there remains an opportunity to self-heal with the formation of new covalent bonds in mechanophores.[85-87]

Besides, mechanophore can be placed in the regions of interest in a material to study the structure-property relationship and the fracture mechanism. Creton and co-workers,[88] incorporated mechanoluminescent bis(adamantly)-1,2-dioxetane into tough elastomers, which consist of double or triple covalent networks. They for the first time confirmed the superb mechanical properties of the double-network materials rely on the scission of prestretched chains and watched them break by detecting mechanoluminescence upon scission of 1,2-dioxetane. Other prospects for mechanophores in polymer science were well reviewed by Craig.[80]

1.4 Aim of the Thesis

In this post doc thesis, we report the use of supramolecular chemistry and biomimetic design to reinforce the mechanical properties of polymeric materials. We also explore polymer mechanochemistry to develop mechanoresponsive materials. The next three chapters will cover the following aspect:

In Chapter 2, we utilized metal-ligand and hydrogen bonding interactions to reinforce and toughen polymers. We fabricated self-healing polymers and conductive nanocomposites based on supramolecular interactions. We also tried to prepare strong and tough hydrogels by simply incorporating hydrophobic monomers.

In Chapter 3, we synthesized spiropyran (SP) mechanophore and explored the correlation between the activation of SP and the supramolecular interactions in bulk. We further demonstrated that SP can be used as a molecular force probe to study the fracture mechanism of polymers. We also tried to explore the force-induced release of target molecules using a 1,2,3-triazole mechanophore.

In Chapter 4, we combined supramolecular chemistry, polymer mechanochemistry, and biomimetic design to prepare mechanoresponsive polymers with strong and tough mechanical properties.

2. Supramolecular Chemistry to Access Strong, Tough, and Self-healing Polymers

2.1 Metal-ligand Interactions and Biomimetic Design to Reinforce and Toughen Polymers

2.1.1 Introduction

As discussed in previous chapter, the combine of supramolecular chemistry and biomimetic design are the two keys to reinforce the mechanical property of polymers. Of particular note is the work by Guan and coworkers. Inspired by titin, they first developed its synthetic analogue by employing dimeric hydrogen bonding system based on *looped* 2-ureido-4[1*H*]-pyrimidone (UPy) motif as the building block of the biomimetic modular domain. The resulting polymers exhibited excellent mechanical properties.[22] To overcome the issues like interchain dimerization in the previous work, they further developed double-closed-loop (DCL) modules of β-sheet[89] and UPy dimer.[25-26]

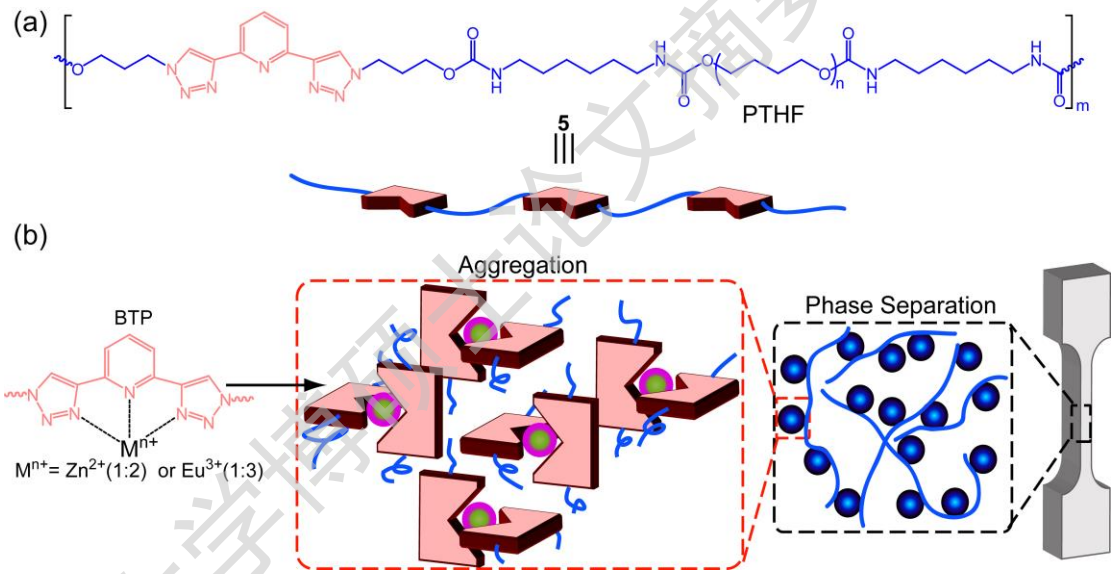

Fig. 2.1 (a) Ligand macromolecule bearing multiple BTP ligand units in the polymer backbone; (b) Schematic illustration showing the metal-ligand complexes phase separate from the linker chains to form "hard phase" domains in the bulk (only the case with Zn^{2+} ions is shown here).

Kinetically labile metal-ligand interactions have been recently widely used to build multi-responsive dynamic materials,[90-98] including optically healable supramolecular polymers based on a photothermal conversion mechanism[97] as well as self-healing polymer coatings using ligand macromolecule bearing ligands in the side chains.[99] Our group has recently developed a new type of ligand macromolecule, where multiple tridentate ligand 2,6-bis(1,2,3-triazol-4-yl)pyridine (BTP) units synthesized via CuAAC click chemistry were incorporated into the polymer backbone by using polytetrahydrofuran (PTHF) linkers (Fig.2.1a).[93] Previously, we have shown that the ligand macromolecule could coordinate with

metal ions such as transition metal ion Zn^{2}+ and/or lanthanide ion Eu^{3}+ to form supramolecular gels in neutral solvents that are sensitive to various stimuli and self-healable. However, the bulk mechanical properties of the metallo-supramolecular polymers have not yet been well understood. In the present work, we are interested in seeing if the dynamic and reversible metal-ligand interactions could be used in the construction of biomimetic polymers that show both robust mechanical properties and adaptability to various stimuli. Of most interest to us are the effects of the nature of the metal-ligand interactions on the load-bearing capacity of the supramolecular domains as well as the adaptive mechanical properties

As illustrated in Fig.2.1b, metal ions first coordinate with the BTP ligand units to form the metal-ligand complexes, which may further phase separate from the soft PTHF segments to form "hard phases" in the bulk. Both the complexes and the resulting hard phases can act as the reversible physical crosslinks in the metallo-supramolecular polymers and mimic the modular domains in biomacromolecules. Upon stretching, the hard phases are expected to be disrupted by fragmentation or by pulling the ligand units, the partially coordinated complexes or the fully coordinated complexes out of the hard phases, acting like sacrificial bonds abundant in biomaterials and releasing the local strain energy. The metal-ligand complexes and their phase segregated hard domains can also be regarded as mechanophores (mechanical sensitive moieties).[1, 76] Together with other fascinating features of the metal ligand complexes (photo- and chemical responsive properties), we are able to demonstrate in this work tough and adaptive properties as well as unique mechano- and thermoresponsive behaviors of metal-ligand based mechanophores in the metallo-supramolecular polymers.

2.1.2 Results and Discussions

Materials Preparation. The synthesis of ligand macromolecule has been reported in our previous publication. BTP ligand can coordinate well with Zn^{2+} and Eu^{3+} to form 1:2 and 1:3 (metal: ligand) complexes,[93] respectively. Here, clean and transparent films with uniform thickness of around 0.5 mm (Fig. 2.2a) were obtained by casting the gels or sols into Teflon casters, followed by careful drying. Samples were denoted as **m:n**, where **m** and **n** denote the theoretical molar percentage of the BTP ligands that bind to Zn^{2+} and Eu^{3+}, respectively. For example, 75:25 means theoretically 75% BTP ligands bind to Zn^{2+} ions and the rest 25% bind to Eu^{3+} ions, 0:0 represents the film made of the ligand macromolecule only. In contrast to literatures,[95-96] mechanically stable and elastomeric films can form for any ratio of Zn^{2+} to Eu^{3+} and any ratio of metal ion to ligand unit tested (no larger than 1), suggesting that our backbone type ligand macromolecule is advantageous to the construction of bulk materials with good mechanical properties.

Mechanical Properties. An example film (**0:100**) made of the ligand macromolecule and stoichiometric amount of Eu^{3+} (all ligand units were bound by Eu^{3+} in a metal to ligand ratio of 1:3) is shown in Fig.2.2a and was stretched by hand. As shown in Fig2.2b, the film can be extended more than 6 times its original length without breaking, displaying remarkable mechanical stability and elastomeric

property. A series of stress-strain experiments was carried out to investigate the mechanical reinforcement imparted by metallo-supramolecular interaction. All metal ion coordinated films displayed fascinating mechanical properties upon external loading. The mechanical responses of films with different stoichiometric ratios of Zn^{2+} : Eu^{3+} are illustrated in Fig.2.2c in terms of engineering stress σ_{Eng} as a function of engineering strain ε_{Eng}. The control sample 0:0 shows a Young's modulus of 4 MPa (calculated by the slope of the curve at very small strain, ε_{Eng} < 20%), an ultimate tensile strength of 3 MPa and a strain at break of 700%. These mechanical data may originate from the physical entanglements of the ligand macromolecule main chain (the entanglement molecular weight of PTHF is about 2,500 g mol-1 [100]) and its polyurethane nature. Nevertheless, the addition of metal ions, either Zn^{2+} or Eu^{3+} or their combinations significantly improved the mechanical performance. Remarkably, the **0:100** film even showed a tensile strength of 18 MPa, a strain at break of 1100% and 4 times increment in the toughness (total area under the stress-strain curve) to the control sample (Fig.2.2d). Furthermore, by varying the ratios of Zn^{2+} : Eu^{3+}, the tensile behaviors can be readily tuned. An obvious trend toward decline of strain at break and concomitant increase of tensile strength is clearly visible as the Zn^{2+} : Eu^{3+} varies from **100 : 0** to **0 : 100**. Apparently, this reinforcement effect can also be regulated by the overall concentration of the metal ions. The mechanical properties of our films are also comparable with those hydrogen bonded thermoplastic elastomers, e.g., UPY based segmented polyurethanes[101] and polyureas.[102] There is a wide range of metal-ligand interactions available, offering the researcher more flexibility to tune the mechanical properties of the bulk materials.

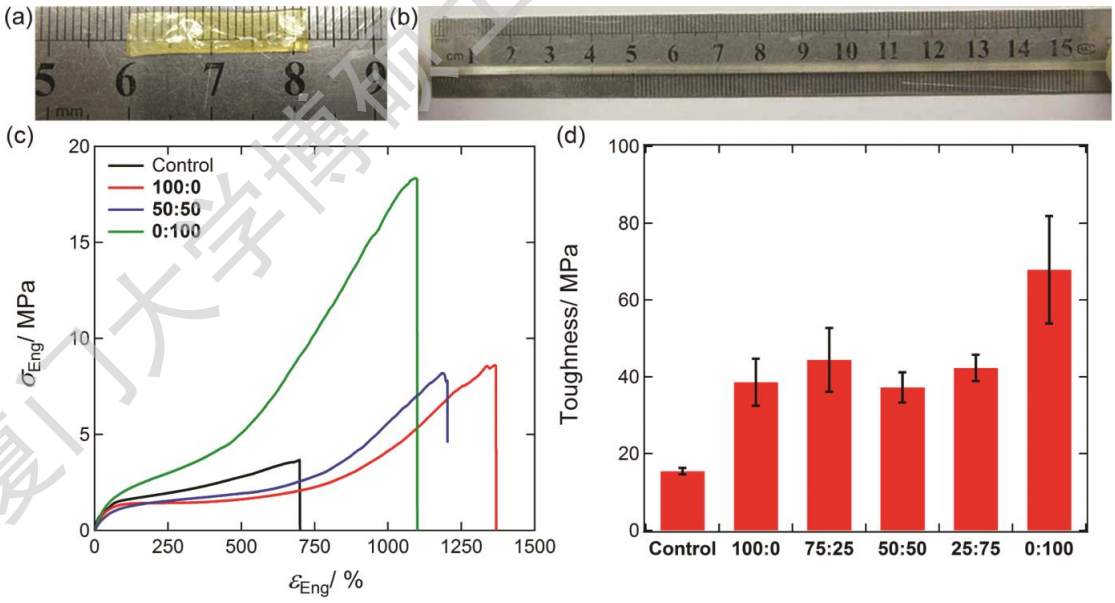

Fig. 2.2 Representative film made of Eu^{3+} (**0:100**) before (a) and after (b) stretching. (c) Stress-strain responses of films with different stoichiometric ratios of Zn^{2+} to Eu^{3+} and (d) the corresponding toughness (area under the stress-strain curves). The number at the bottom of the *x*-axis in (d) is the stoichiometric ratio of Zn^{2+}: Eu^{3+}. The control sample **0:0** denotes film made from ligand macromolecule only.

The stress-strain curves all exhibit sigmoid shape characteristic for elastomeric polymers and are typically composed of three regions. A linear elastic region at small $\varepsilon_{Eng,}$ typically <100% (Region I), and the stress response are due to the reduced entropy of the linker polymer chains. After the pseudo yield point, there is an intermediate region (Region II), in which the stress increases slowly with strain. The breaking of the "hard phase" modular domains and/or the disruption of the intrachain and interchain metal-ligand complexes are expected to dominate in this region. In this intermediate region the force across the cross section is almost constant for 100% Zn^{2+} containing films and as a general trend the higher Zn^{2+} ratio the more flattened Region II appears. This is possibly due to the more mechanically labile nature of the Zn: BTP complex and/or its hard phase as compared to the Eu^{3+} counterparts. Further stretching leads to a stiffer upturn of stress (Region III), which may result from the limited chain extensibility or the strain induced crystallization of the PTHF block as the progressive breaking and/or dissociation non-covalent domains (*vide infra*) and alignment of polymer chains continue.[103] It should be noted that dynamic balance of disruption and rebuild of metal-ligand complexes may persist during stretching. The mean toughness values of the various films from three independent measurements are illustrated in Fig2.2d. It is evident that upon the complexation with metal ions the toughness is drastically increased, especially when 100% Eu^{3+} ions was introduced. However, for the four Zn^{2+} containing films the toughness values are within the experimental error, indicating that Zn^{2+} has a significant effect on the toughness. Collectively, we infer the 100% Eu^{3+} (**0:100**) film is stronger and more mechanically stable than the Zn^{2+} containing ones. By using metal-ligand interactions, we are able to construct supramolecular polymers with variable biomimetic high tensile strength, toughness and tensile strain.

Microphase Separation. To gain further insight into the superb mechanical properties of the metallo-supramolecular films, we then turned to study the microphase separation and the thermal behaviors. Small angel X-ray scattering (SAXS) measurements were first performed on the films with various Zn^{2+}: Eu^{3+} ratios and ratios of metal to ligand at room temperature. No diffraction peak is identified for the control sample **0:0** (Fig.2.3a). A primary Bragg diffraction peak at around q_1 = 0.50 nm^{-1} ($d_1 = 2\pi/q_1 \approx 12$ nm) is identified for all metal ion containing films, which is related to the average distance between the metal-ligand "hard phase" domains. This result is consistent with previous report on metallo-supramolecular systems based on chain end type ligand macromonomer.[94] We denote this peak as "q_1 peak" in the following discussions. Interestingly, by varying Zn^{2+} : Eu^{3+} ratios at a stoichiometry of metal to ligand of 1, the q_1 peak slightly shifts to higher q as Eu^{3+} content was increased, whereas the peak shape was almost unchanged. For films containing only Zn^{2+} or only Eu^{3+}, the q_1 peak slightly shifts to lower q as the metal ion concentration was decreased. Thus, more bulky or denser "hard phases" are expected for lower Zn^{2+} : Eu^{3+} ratios and higher metal ion contents. In addition, the q_1 peak of the **25:0** and **0:25** films are not as sharp as their counterparts, indicating less interdomain interference for low metal ion concentrations. No long range ordered structures existed here as revealed by the lack of subsequent scattering peaks at